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Adhesive Systems for Pesticide Delivery Through Plant Stems

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Abstract: An adhesive polymeric system for delivering pesticides through the stem of plants has been developed using a polymeric adhesive membrane with penetration enhancers. The active agent, imidacloprid, 1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine, incorporated in either acrylic adhesive polymer or natural rubber membrane was effectively absorbed through the stem of the model plant, eggplant (*Solanum melongena*), at a controlled rate of penetration. The penetration rate across the cuticular membrane was enhanced by 5·1 times and 2·4 times with *l*-menthol and *d*-limonene, respectively, incorporated in the polymer membrane as penetration enhancers. Correspondingly, the acrylic adhesive pesticide patch with *l*-menthol provided the highest insecticidal activity. The present adhesive transepidermal pesticide delivery system can deliver the active agent directly to the target site as well as minimizing the excess amount of the active agent wasted throughout the non-target environment.

Key words: adhesive pesticide patch, penetration enhancer, transepidermal absorption, imidacloprid, insecticidal activity

1 INTRODUCTION

There is little question that we may face a higher risk from pesticides if we increase the consumption of conventional pesticide formulations such as sprays and powders. The more we apply pesticides for controlling pests, the more hazardous compounds move throughout the environment, soil, water and biota. A literature survey indicates that less than 0·1% may reach target pests from a conventional spray formulation.[1] For solving the competing problems of food production versus environmental pollution, we may need to develop effective means of delivering the pesticide more directly to the target sites and insects.

Recently, controlled release technologies have been increasingly applied to improve the efficacy of pesticides.[2,3] The active pesticidal agent, incorporated in a wide variety of polymeric devices of different geometries, including microcapsules,[4] hollow fibres,[5] granules[6] and tapes,[7] is released for a prolonged period of time near to the site of action. Although the controlled release formulations developed currently utilize the active agent more effectively than conventional formulations, we can neither eliminate the excess pesticide distributed throughout the non target environment nor control the rate of absorption into the target plant.

This paper describes an adhesive polymeric delivery system for pesticides, the active agent from which is absorbed through the surface of the stem of plant at a programmed rate. The active agent can then reach the target site following the upward translocation of water in the plant body. Since no active agent moves into non target environment during travel in the plant body, the excess amount of pesticide wasted can be minimized. The pesticide patch is also effective in avoiding bursting release and rapid washout due to unexpected weather

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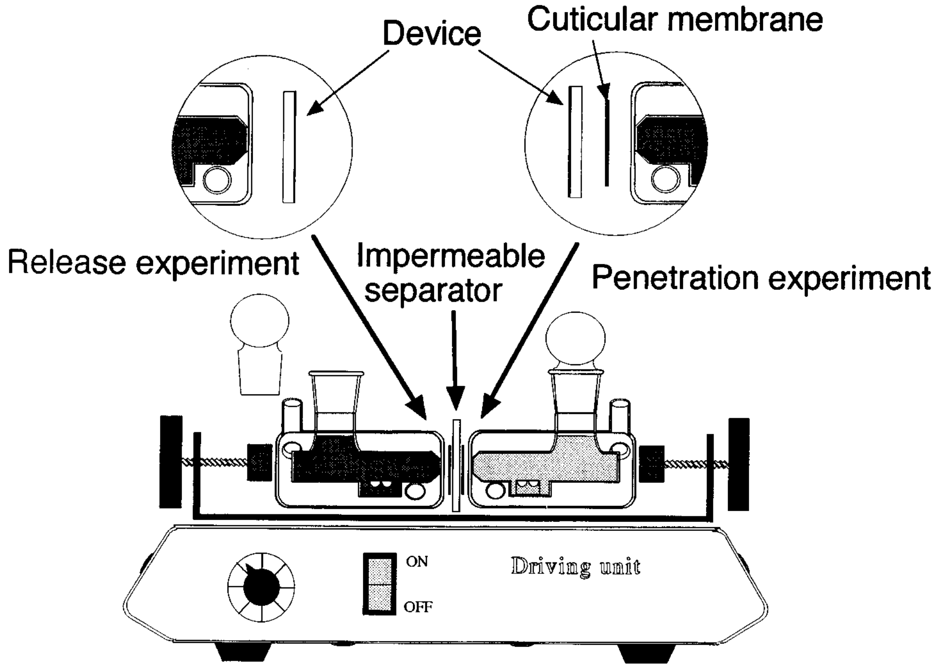

Fig. 1. Side-by-side diffusion cell system for measuring release rate of pesticide from the delivery device (left half-cell) and permeability across cuticular membrane isolated from plant (right half-cell). The effective area for mass transport and volume of compartment are 0·20 cm^2 and 5·0 ml, respectively. The thickness of the diffusion boundary layer formed on the surface of membrane was approximately 30 μm at the rotation speed of stirrer of 17 revolutions per second.[8]

conditions. Therefore the adhesive polymeric delivery of pesticides through the stem of plant assures the programmed efficacy of pest control under various environmental conditions.

2 MATERIALS AND METHODS

2.1 Pesticide patch development

Imidacloprid, 1-(6-chloro-3-pyridylmethyl)-*N*-nitro-imidazolidin-2-ylideneamine (Nihon Bayer Agrochem, Ibaraki, Japan), as the model pesticide compound is incorporated homogeneously in the matrix of polymeric membrane made from either acrylic adhesive polymer (Wako Chemical, Osaka, Japan) or natural rubber (Yutoku Pharmaceuticals, Kashima, Saga, Japan), together with an enhancing agent for penetration. Since the active agent, a hydrophilic compound with 0·51 g $litre^{-1}$ water solubility at 20°C, penetrates, through the cuticular membrane of the plant stem with difficulty, an appropriate penetration-enhancing agent may be incorporated in the polymer matrix. Once penetrated

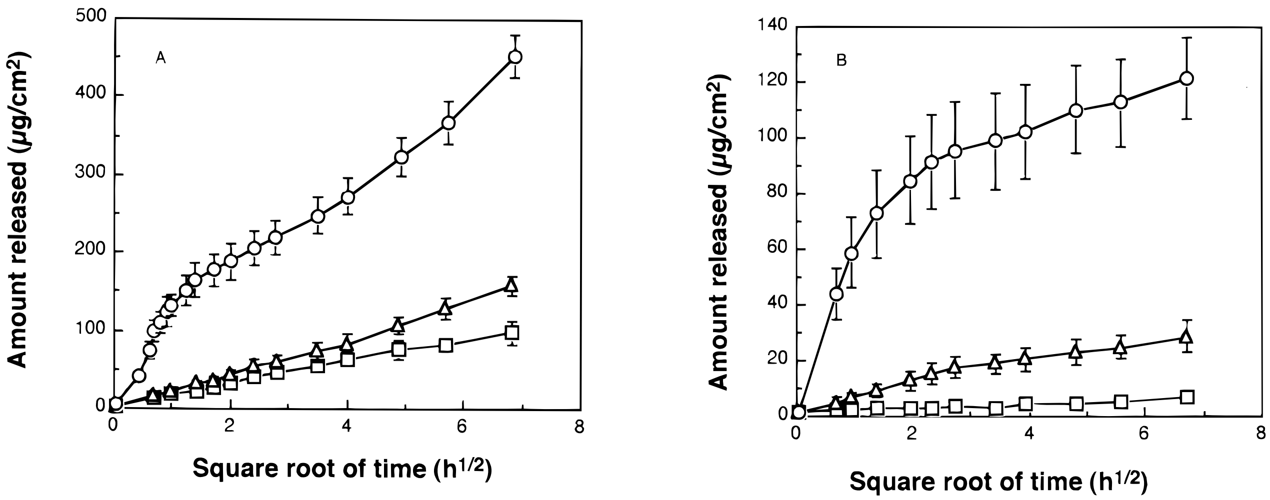

Fig. 2. Cumulative amount of imidacloprid released from adhesive pesticide delivery systems as a function of the square root of time. (A) acrylic polymer device and (B) natural rubber device (without enhancers). Loading dose of the active agent: (○) 18%, (△) 5%, (□) 2%. Error bars (SD) are shown for one set of data (n = 5).

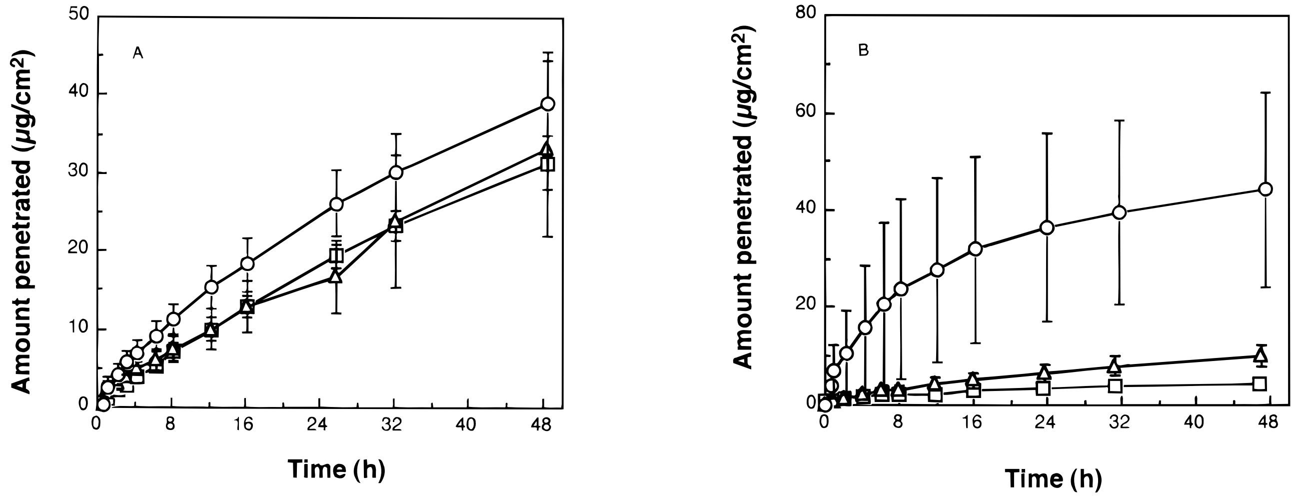

Fig. 3. Cumulative amount of imidacloprid penetrating across the cuticular membrane of the stem of eggplant following adhesive pesticide delivery. (A) acrylic polymer device, (B) natural rubber device. Loading dose of the active agent: (○) 18%, (△) 5%, (□) 2% (without enhancers). Error bars (SD) are shown for one set of data ($n = 5$).

through the surface cuticular membrane, the pesticide can move up throughout the plant following the upward translocation of water. In this study, *l*-menthol or *d*-limonene was added to the polymer matrix as a possible enhancing agent for imidacloprid. Mixed homogeneously at 45°C, the mixture of the active agent (0·5–0·92 g), the polymeric material (4 g), the enhancer (0–1·23 g) and the solvent, toluene (6 ml), was spread onto the surface of the release liner, PET (polyethylene terephthalate) film. When dried completely, after about 5 h, the device was backed with high density polyethylene membrane, dark-colored for light protection. The device was then cut into 1·6 × 3·2 cm size. The thickness of polymer membrane which contained the pesticide was 30 μm for the polyacrylic membrane device and 100 μm for the natural rubber device, respectively. The loading dose of the active agent varied within the range 2 to 18% by weight. The pesticide patches were then stored in the protective package until use.

The release rate of the active agent from the delivery system was measured in the side-by-side membrane permeation cell without cuticular membrane attached (left half-cell in Fig. 1) at 25°C. The elution medium was distilled water. The flow characteristics in the diffusion cell had been fully investigated previously.[8] The penetration rate of the active agent across the cuticular membrane of eggplant (*Solanum melongena* L. cv. Senryo No. 2, eight weeks after germination) was measured in the membrane penetration cell system by attaching the cuticular membrane isolated from the stem of eggplant to the surface of the pesticide patch (right half-cell in Fig. 1). The cuticular membrane of the eggplant was enzymatically separated by modifying the approach for cucumber cuticular membrane used by Oohori and Ibashi.[9] After keeping a piece of eggplant stem (approximately 0·5 cm diameter × 1·5 cm length) in the enzyme solution[9] for 48 h, the cuticular membrane was smoothly isolated from the stem of the plant. The cuticular membrane was then mounted in the side-by-side diffusion cell system for measuring the rate of penetration of the pesticide. At predetermined time intervals 100 μl of receptor sample was withdrawn to measure the concentration and the same amount of fresh water was added to the receptor solution. Both the penetration and release experiments were carried out for 48 h. The concentration of the active agent, imidacloprid, was assayed by HPLC.[10]

2.2 Insecticidal activity

The acrylic adhesive pesticide patch containing 15% imidacloprid by weight was applied to the surface of the stem of the eggplant approximately 5 cm above the ground level. The average effective surface area when placed on the plant was 3·0 cm². Prior to the application of patch, 10 adult aphids, *Aphis gossypii*, (Glov.) were placed on both sides of a leaf and covered with a hemispherical net to avoid runaways. The total number of aphids, both adults and nymphs reproduced, was counted every 24 h during application. The temperature (25°C), humidity (60%) and light–dark cycle (12 h/12 h) were controlled in a computer-controlled weather chamber (NK System BIOTRON NC350, Nihon Ika Kikai, Co., Tokyo, Japan).

3 RESULTS AND DISCUSSION

3.1 Release and penetration profiles

The release profile of imidacloprid from the delivery systems with low loading dose (2 and 5%) followed a

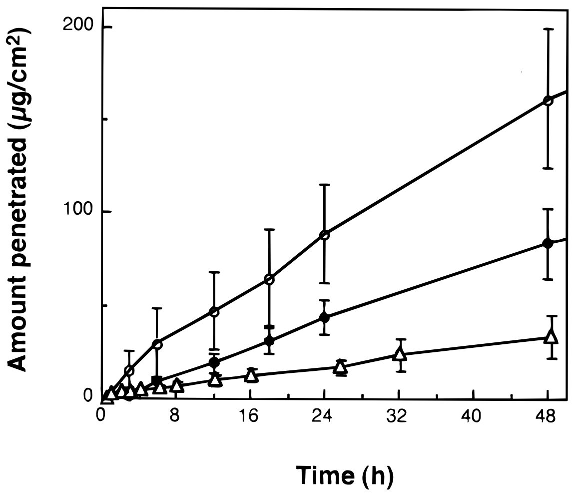

Fig. 4. Effect of penetration-enhancing agents on the cumulative amount of imidacloprid across cuticular membrane of the stem of eggplant. Loading dose of the active agent: 5% by weight Acrylic polymer device. Concentration of enhancers 20% by weight. Key: (○) *l*-menthol ($n = 3$), (●) *d*-limonene ($n = 3$), (△) no enhancer ($n = 6$). Error bars: SD.

typical diffusion-controlled profile, in that the cumulative amount released was approximately proportional to the square root of time.[11] However, the release rate from high loading dose device (18%) showed a bi-phasic profile, initial bursting release and thereafter a diffusion-controlled time-dependent release (Fig. 2).

The cumulative amount of the active agent penetrating across the cuticular membrane of the stem of eggplant was influenced by the material of the polymeric membrane used (Fig. 3); the acrylic polymer device showed relatively constant penetration rate independent of the loading dose, while the penetration profile for the natural rubber device was strongly influenced by the loading dose. This finding may indicate that the rate of absorption of the pesticide through the plant epidermis can be controlled by the polymeric materials as well as by the loading dose of the active agent incorporated. The acrylic polymer device provided a penetration rate appreciably higher than the rubber device, indicating that the acrylic polymer is preferable as the polymeric material with respect to penetration enhancement for imidacloprid. This is probably due to the improved partitioning of imidacloprid on the surface of the cuticular membrane. The cumulative amounts of the active agent penetrating during the first 48 h for the acrylic polymer device with 2, 5 and 18% loading dose were, respectively, 3·3, 4·7 and 12 times smaller than the amount released. This finding may suggest that the rate-limiting step for the pesticide absorption across the stem of the plant resides in the diffusion process across the cuticular membrane. When the penetration enhancers were incorporated in the polymer membrane, the rate of penetration of imidacloprid across the cuticular membrane of eggplants was appreciably promoted; acrylic adhesive devices containing the enhancers, *l*-menthol or *d*-limonene, increased the rate of penetration respectively 5·1 times and 2·4 times over that without enhancers (Fig. 4). However, the effect of *l*-menthol and *d*-limonene on the release rate was found to be insignificant.[10] Therefore the penetration enhancers may

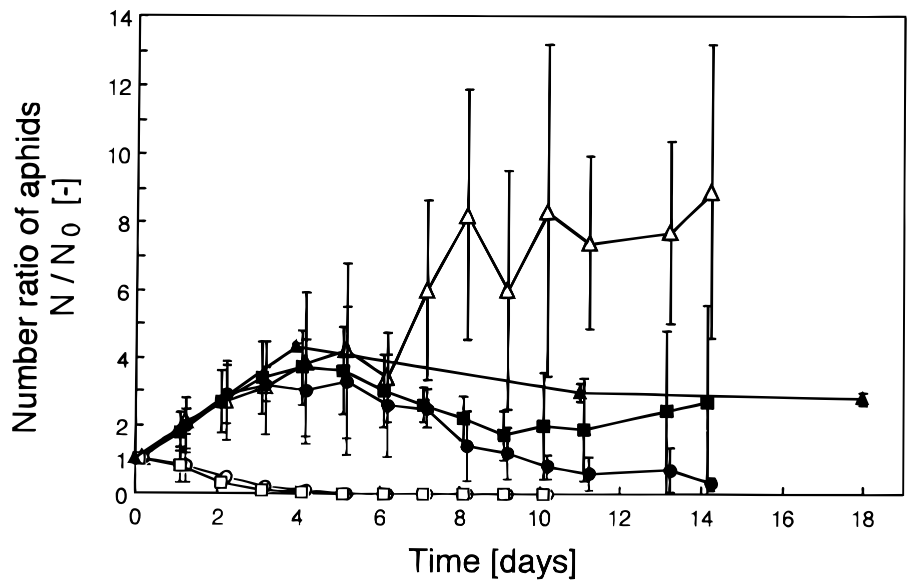

Fig. 5. Time variation of number ratio of aphids surviving following acrylic adhesive delivery of imidacloprid through the stem of eggplant. Ten adult aphids, *Aphis gossypii*, were initially placed on both sides of leaf ($N_0 = 10$). Loading dose of active agent: 15% by weight (approximately 3 mg per patch); concentration of enhancer: 20% by weight ($n = 3$ per experiment. Error bars: SD.) (△) Control, no device ($n = 6$) or placebo device ($n = 6$) applied, upper and lower surfaces, (▲) no enhancer, upper and lower surfaces ($n = 6$), (●) upper surface, *d*-limonene, (■); lower surface, *d*-limonene, (○) upper surface, *l*-menthol, (□) lower surface, *l*-menthol.

improve the partitioning and diffusion of imidacloprid in the cuticular membrane of the stem of eggplant.

Clear insecticidal activity was observed for the acrylic polymer devices (Fig. 5). The device containing *l*-menthol as the enhancer showed the highest mortality of aphids on the leaf; the aphids were completely controlled four days after application. However, it took two weeks or more for the device with *d*-limonene to achieve complete mortality. We did not observe any insecticidal activity in placebo devices which contained no active agent, with or without enhancers. The pesticide patch without enhancer (closed triangles in Fig. 5) showed mortality lower than the device with enhancers but higher than the placebo patch, although the difference in efficacy is not significant. The mortalities with the present pesticide patches correlate excellently with the penetration rate of the active agent through the cuticular membrane shown in Fig. 4, indicating that the diffusion experiment using isolated cuticular membrane may be useful in screening possible enhancers for pesticides. The pesticide delivery systems developed in this study did not cause any phytotoxic symptoms on tested plants.

3.2 Comparison with conventional formulation

The amount of imidacloprid to control aphids on eggplants is usually recommended to be 10 to 20 mg per plant, three times per season, for granule formations in the vicinity of the root.[12] The total quantity of the active agent consumed is then 30 to 60 mg per plant. On the other hand, the pesticide patch with 15% loading dose used in this study contains approximately 3 mg of the active agent in each patch. The strong insecticidal activity of the present pesticide patch suggests that the adhesive pesticide delivery through the stem of plant is an efficient novel approach for the application of pesticides, although large-scale field tests have yet to be carried out. The adhesive pesticide delivery system is therefore effective in protecting both plants and environment by achieving direct targeting and a resulting decrease in pesticide consumption.

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